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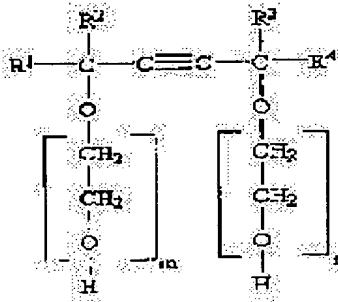
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### (54) COLOR INK-JET RECORDING

#### (57)Abstract:

PROBLEM TO BE SOLVED: To a method for color ink-jet recording capable of preventing bleed during color printing and offering a sharp and clear image.

SOLUTION: This color ink-jet recording method comprises using inks of plural colors composed of at least water, a dye, a hydrophilic high-boiling low volatile solvent, a polyhydric lower alkyl ether and an acetylene shown by the formula (R1, R2, R3 and R4 are each independently 1-6C alkyl group; n+m is 0-30). In this case, a block ink and/or a color ink contains a gold-containing ink as a colorant. Printing of high image quality free from bleeding and feathering can be carried out irrespective of kinds of ordinary papers and during color recording and monochromic recording only by block.



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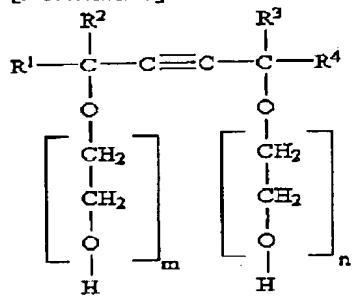
CLAIMS

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[Claim(s)]

[Claim 1] The color ink-jet record method which is the color ink-jet record method using the ink of two or more colors which come at least to contain water, a color, a hydrophilic quantity boiling point low volatile solvent, polyhydric-alcohol low-grade alkyl ether, and the acetylene glycol expressed with the following general formula, and is characterized by black ink and/or color ink containing an auriferous color as a coloring agent.

[Formula 1]



(Here, R1, R2, R3, and R4 express independently the alkyl group of carbon numbers 1-6, respectively, and n+m expresses 0-30)

[Claim 2] The color ink-jet record method according to claim 1 that color ink is characterized by the coloring agent of black ink containing  $-\text{COO}-$  as a functional group, including an auriferous color.

[Claim 3] The color ink-jet record method according to claim 1 that color ink is characterized by black ink containing a pigment in the state of distribution, including an auriferous color.

[Claim 4] The color ink-jet record method which comes to contain the acetylene glycol expressed with the aforementioned general formula 7 - 12wt% in polyhydric-alcohol low-grade alkyl ether in the aforementioned ink in 0.5 - 1.2wt%.

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## DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] this invention relates to the formation method of a color picture, and the color ink-jet record method of having used two or more primary color record liquid in more detail.

[0002]

[Description of the Prior Art] As a result of in the color ink-jet record which generally piles up and prints each color of yellow, a Magenta, and cyanogen the ink which are liquids carrying out color mixture mutually or flowing out, bleeding, a mustache, etc. occur and the big technical problem that a quality of printed character deteriorates exists.

[0003] Then, in order to solve the above-mentioned technical problem conventionally, the surface tension of the record liquid of each color which forms a color picture should set at 20 degrees C like JP,60-197778,A. It is within the limits of 30 – 60 dyn/cm, and the fixing business time of the record liquid of each color to a recorded material and a bleeding degree are made equal by using that to which the surface tension of the record liquid of each color was equal, and the method of suppressing degradation of a color picture is proposed. However, by the method using the aforementioned record ink, the degree of bleeding of a record object does not decrease and cannot become a means to improve picture degradation. Moreover, in color printing containing especially the color mixture section, the bleeding of the ink between black colors occurs and the yet sufficiently high definition color ink-jet record method cannot be realized.

[0004]

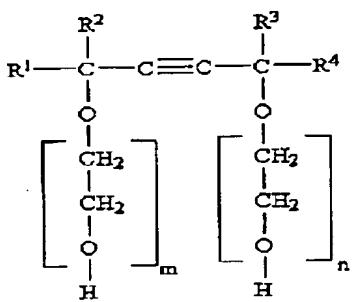
[Problem(s) to be Solved by the Invention] Then, especially the place made into the purpose of this invention is to offer the color ink-jet record method that the bleeding at the time of color printing is prevented, and a sharp and clear picture can be offered. Furthermore, it is not based on the kind of regular paper, but bleeds also at the time of color record and monochrome record of only black, and is in performing beardless high definition printing.

[0005]

[Means for Solving the Problem] In order that this invention persons may solve the above-mentioned technical problem, as a result of repeating examination wholeheartedly, at least Water, In the color ink-jet record method using the ink of two or more colors which come to contain a color, a hydrophilic quantity boiling point low volatile solvent, polyhydric-alcohol low-grade alkyl ether, and the acetylene glycol expressed with the following general formula When black ink and/or color ink contained an auriferous color as a coloring agent, the bleeding between black ink color ink was suppressed, and it found out that a sharp and clear picture was acquired.

[0006]

[Formula 2]



[0007] (Here, R1, R2, R3, and R4 express independently the alkyl group of carbon numbers 1–6, respectively, and  $n+m$  expresses 0–30)

When the coloring agent of black ink contains  $-\text{COO}-$  as a functional group in the further above-mentioned case, the bleeding between black ink color ink is prevented more effectively.

[0008] Moreover, when black ink contains a pigment in the state of distribution, the higher bleeding prevention effect is realized.

[0009] Furthermore, bleeding, a mustache, etc. at the time of monochrome printing were suppressed, and this invention persons found out that a high definition picture was acquired, when black ink or color ink contained an auriferous color as mentioned above.

[0010]

[Embodiments of the Invention] this invention is explained in detail. The auriferous color which the color ink used by the color ink-jet record method of this invention contains at least water, a color, a hydrophilic quantity boiling point low volatile solvent, polyhydric-alcohol low-grade alkyl ether, and the acetylene glycol expressed with the above-mentioned general formula, and has a transition-metals atom in a molecule as a color is used. In this case, although the above-mentioned bleeding prevention effect is realized even if it uses an auriferous color independently as a coloring agent, the same effect is acquired, when two or more auriferous colors are included in ink or an auriferous color and a non-auriferous color are mixed and included.

[0011] this invention person etc. reasons as follows the reason for having the effect that an auriferous color suppresses color bleeding as mentioned above. That is, although an auriferous color is divided roughly into what has transition metals at the center of a molecule like a phthalocyanine, and the thing which the metal has configurated for example, in azo combination etc., in any case, generally the metal atom circumference has a high hydrophobic property, and since it is a water soluble dye, a hydrophilic radical exists in addition to the metal atom circumference. Therefore, generally compared with a non-auriferous color, it is considered by a hydrophilic target and the canal-interaction for an auriferous color to have the strong cohesive force between molecules. When ink is printed on a recorded material, the auriferous color with the strong interaction between molecules succeeds in condensation structure, and in order to prevent other colors etc. invading, the high bleeding prevention effect is demonstrated.

Moreover, since the cohesive force between molecules is strong, it is thought that it is hard to produce bleeding, a mustache, etc. also at the time of monochrome printing.

[0012] As an auriferous \*\*\*\*\* non-auriferous coloring agent used in the color ink-jet record method of this invention, pigments (graft carbon etc.) which processed the pigment front face by the resin etc. further, such as direct dye, acid dye, the food color, basic dye, a disperse dye, a vat dye, a solubilized vat dye, a reaction disperse dye, fat dye and an inorganic pigment (carbon black), and an organic pigment (insoluble azo pigment, soluble azo pigment, a phthalocyanine system pigment, an isoindolinone system pigment, a Quinacridone system pigment, \*\* RINON, perylene system pigment), can be used In this, especially a water soluble dye is desirable on the performance of ink. Specifically C. — I. direct red 2, 4, 9, 16, 23, 26, 31, 39, 62, 63, 72, 75, 76, 79, 80, 81, 83, 84, 89, 92, 95, 111, 173, 184, 207, 211, 212, 214, 218, 221, 223, 224, 225, 226, 227, 232, 233, 240, 241, 242, 243, 247, C.I. direct violet 7, 9, 47, 48, 51, 66, 90, 93, 94, 95, 98, 100, 101, C.I. direct yellow 8, 9, 11, 12, 27, 28, 29, 33, 35, 39, 41, 44, 50, 53, 58, 59, 68, 86, 87, 93, 95, 96, 98, 100, 106, 108, 109, 110, 130, 132, 142, 144, 161, 163, C.I. direct blue 1, 10, 15, 22, 25, 55, 67, 68, 71, 76, 77, 78, 80, 84, 86, 87, 90, 98, 106, 108, 109, 120, 151, 156, 158, 159, 160, 168, 189, 192,

193, 194, 199, 200, 201, 202, 203, 207, 211, 213, 214, 218, 225, 229, 236, 237, 244, 248, 249, 251, 252, 264, 270, 280, 288, 289, 291, C.I. direct black 9, 17, 19, 22, 32, 51, 56, 62, 69, 77, 80, 91, 94, 97, 108, 112, 113, 114, 117, 118, 121, 122, 125, 132, 146, 154, 166, 168, 173, 199, C.I. acid red 35, 42, 52, 57, 62, 80, 82, 111, 114, 118, 119, 127, 128, 131, 143, 151, 154, 158, 184249, 254, 257, 261, 263, 266, 289, 299, 301, 305, 336, 337, 361, 396, 397, and C.I. acid violet 5, 34, 43, 47, 48, 90, 103, 126, C.I. acid yellow 17, 19, 23, 25, 40, 42, 44, 49, 50, 61, 64, 76, 79, 105, 110, 127, 135, 143, 151, 159, 169, 174, 190, 195, 196, 197, 199, 218, 219, 222, 227, and C.I. acid blue 9, 25, 40, 41, 62, 72, 76, 78, 80, 82, 92, 106, 112, 113, 120, 127:1, 129, 138, 143, 175, 181, 205, 207, 220, 221, 230, 232, 247, 258, 260, 264, 271, 277, 278, 279, 280, 288, 290, 326, C.I. acid black 7, 24, 29, 43, 48, 52:1, 172, C.I. reactive red 3, 13, 17, 19, 21, 22, 23, 24, 29, 35, 37, 40, 41, 43, 45, 49, 55, and C.I. reactive violet 1, 3, 4, 5, 6, 7, 8, 9, 16, 17, 22, 23, 24, 26, 27, 33, 34, C.I. reactive yellow 2, 3, 13, 14, 15, 17, 18, 23, 24, 25, 26, 27, 29, 35, 37, 41, 42, C. — I. reactive blue 2, 3, 5, 8, 10, 13, 14, 15, 17, 18, 19, 21, 25, 26, 27, 28, 29, 38, and C.I. reactive black 4, 5, 8, 14, 21, 23, 26, 31, 32, 34, and C.I. basic red 12, 13, 14, 15, 18, 22, 23, 24, 25, 27, 29, 35, 36, 38, 39, 45, 46, C.I. basic violet 1, 2, 3, 7, 10, 15, 16, 20, 21, 25, 27, 28, 35, 37, 39, 40, 48, C. — I. basic yellow 1, 2, 4, 11, 13, 14, 15, 19, 21, 23, 24, 25, 28, 29, 32, 36, 39, 40, C.I. basic blue 1, 3, 5, 7, 9, 22, 26, 41, 45, 46, 47, 54, 57, 60, 62, 65, 66, 69, 71, C. I. basic black 8 etc. is mentioned.

[0013] As a content of the auriferous \*\*\*\*\* auriferous coloring agent in an ink composition part, in consideration of the printing concentration of a record object, clogging, a regurgitation property, etc., it is the range of 0.2 – 15wt% in a solid content as the sum total of all the coloring agents in ink, and is the range of 0.5 – 10wt% preferably.

[0014] As a hydrophilic quantity boiling point low volatile solvent used for this invention A glycerol, ethylene glucohol, a diethylene glycol, a triethylene glycol, A propylene glycol, a dipropylene glycol, a hexylene glycol, The polyhydric alcohol of high boiling point low volatility, such as a polyethylene glycol and a polypropylene glycol, is used. In addition, an N methyl 2-pyrrolidone, 1, 3-dimethyl imidazolidinone, Monoethanolamine, N, and N-dimethylethanolamine, N, and N-diethyl ethanolamine, Water-soluble organic solvents, such as nitrogen-containing organic solvents, such as an N-n-butyl diethanolamine, tri-isopropanolamine, and a triethanolamine, can be added in the range which bleeding of printing does not produce. A diethylene glycol, a glycerol, etc. are especially desirable. although it is common knowledge that these hydrophilic quantity boiling point low volatile solvents are added as a moisturizer for clogging prevention etc. — the greatest effect as an indispensable component of this invention — a member — it is in relief of pervasion nature the case where volatile components, such as water, evaporate on the inside of a head, an ink supply way, etc. by unusual situation generating especially according to failure of a printer etc. — the member of polyhydric-alcohol low-grade alkyl ether — pervasion nature is eased

[0015] moreover — as the desirable example of the polyhydric-alcohol low-grade alkyl ether used for this invention — monochrome, JI, and a triethylene glycol C — one to 6 alkyl ether, the triethylene-glycol monobutyl ether, the diethylene-glycol monobutyl ether, a diethylene glycol monoethyl ether, the diethylene-glycol monomethyl ether, the propylene-glycol monobutyl ether, etc. are mentioned more preferably, and it is the triethylene-glycol monobutyl ether most preferably This addition is 7 – 10wt% preferably [ that it is 7 – 12wt% ] and more preferably.

[0016] Moreover, the acetylene glycol expressed with the above-mentioned general formula must be contained in the ink used by this invention. If the desirable example of an acetylene glycol is given, it will be as in Table 1.

[0017]

[Table 1]

|       | R <sup>1</sup> | R <sup>2</sup> | R <sup>3</sup> | R <sup>4</sup> | n + m |
|-------|----------------|----------------|----------------|----------------|-------|
| No. 1 | iso-ブチル        | メチル            | メチル            | iso-ブチル        | 10    |
| No. 2 | iso-ブチル        | メチル            | メチル            | iso-ブチル        | 3.5   |
| No. 3 | エチル            | メチル            | メチル            | エチル            | 10    |
| No. 4 | メチル            | メチル            | メチル            | メチル            | 0     |
| No. 5 | エチル            | メチル            | メチル            | エチル            | 0     |
| No. 6 | iso-ブチル        | メチル            | メチル            | iso-ブチル        | 0     |

[0018] The acetylene glycol of No.1 in Table 1 is the most desirable.

[0019] These acetylene glycols can use what is marketed, for example, can use ORUFIN E1004, E1010, and STG, SAFI Norian 82 (manufacturer : Air Product and Chemicals, Inc., a selling agency : Shin-Etsu Chemical Co., Ltd.), etc.

[0020] The addition of an acetylene glycol is 0.5 – 1wt% preferably [ that it is 0.5 – 1.2wt% ] and more preferably.

[0021] By using combining polyhydric-alcohol low-grade alkyl ether and an acetylene glycol with the above-mentioned addition, quick-drying [ of an ink constituent ] is improved and degradation of the quality of printed character by bleeding, color mixture, etc. can be prevented. Furthermore, although the phenomenon which erodes the resin which constitutes a recording head and ink passage will often be observed if polyhydric-alcohol low-grade alkyl ether is used by independent [ it ], it is combining with an acetylene glycol and such an erosion phenomenon can also be prevented. furthermore, the above-mentioned hydrophilic quantity boiling point low volatile solvent — polyhydric-alcohol low-grade alkyl ether — receiving — more than the 50wt% — the effect is more improvable by adding

[0022] In addition, in the record ink used for the ink set for color ink-jet record of this invention, a well-known dispersant, a surfactant, a viscosity modifier, a surface tension modifier, a specific resistance modifier, pH modifier, an antioxidant, an antifungal agent, a chelating agent, etc. can be added if needed conventionally.

[0023] Although the contents in the ink composition part of these various additives differ according to the purpose, as for an excessive amount, it is desirable to foam and to use it in 0.001 – 5wt% from causes, such as a deposit and shelf-life degradation, and a bird clapper.

[0024] Although the content of the water used by this invention is determined in the latus range depending on the kind of the above-mentioned solvent component, additive, etc., a content, and the property of ink for which it asks, in the record liquid whole quantity, generally it is 40 – 95wt%, and the range of it is 65 – 95wt% more preferably.

[0025]

[Example] An example and the example of comparison are used for below, and the color ink-jet record method of this invention is further explained to it.

[0026] Composition of the ink used for the evaluation mentioned later first is summarized in Table 2. the number in Table 2 — all — a weight criteria % display — it is — a residue — the whole — 100% — \*\* — it means adding pure water so that it may become After mixing each component of Table 2 and agitating and dissolving at 25 degrees C for 2 hours, using the membrane filter (Advantech registered trademark) of the diameter of 0.8 micrometer, the pressure filtration of kg [ 2 / / ] was carried out by the pressure of 2 cm, and each ink was obtained. In addition, although both the direct blacks 154 and direct blacks 90 of front Naka are non-auriferous colors, the former has –COO– as a functional group and the latter does not have them. Moreover, since carbon black has mainly embellished the front face with –COO–, it is making the stable distributed state in ink, without otherwise adding a dispersant etc.

[0027]

[Table 2]

|                  |              | ブラック インク |       |       |       |
|------------------|--------------|----------|-------|-------|-------|
|                  |              | インクB1    | インクB2 | インクB3 | インクB4 |
| 含金染料             | アッシュブラック43   | 2.0      |       |       |       |
| 非含金染料            | ダイレクトブラック90  |          | 2.0   |       |       |
|                  | ダイレクトブラック154 |          |       | 2.0   |       |
| 表面処理剤            | カーボンブラック     |          |       |       | 2.0   |
| TEGmBE           |              | 10.0     | 10.0  | 10.0  | 10.0  |
| Olfine STG       |              | 0.8      | 0.8   | 0.8   | 0.8   |
| グリセリン            |              | 9.0      | 9.0   | 9.0   | 9.0   |
| 2-ヒドリドン          |              | 4.0      | 4.0   | 4.0   | 4.0   |
| TEA              |              | 0.9      | 0.9   | 0.9   | 0.9   |
| Proxel XL-2      |              | 0.3      | 0.3   | 0.3   | 0.3   |
| H <sub>2</sub> O |              | 残量       | 残量    | 残量    | 残量    |

|                  |              | イエローインク |       |       | マゼンタインク |       | シアンインク |       |       |
|------------------|--------------|---------|-------|-------|---------|-------|--------|-------|-------|
|                  |              | インクY1   | インクY2 | インクY3 | インクM1   | インクM2 | インクC1  | インクC2 | インクC3 |
| 含金染料             | ダイレクトイエロー39  | 3.0     |       |       | 2.0     |       | 3.0    |       |       |
|                  | アッシュレッド184   |         |       |       |         |       | 3.0    |       |       |
|                  | ダイレクトブルー199  |         |       |       |         |       | 3.0    |       |       |
|                  | ダイレクトブルー202  |         |       |       |         |       | 3.0    |       |       |
| 非含金染料            | アッシュドイエロー105 | 3.0     |       |       | 1.0     |       | 3.0    |       |       |
|                  | ダイレクトレッド16   |         |       |       |         |       | 3.0    |       |       |
|                  | ダイレクトブルー120  |         |       |       |         |       | 3.0    |       |       |
| TEGmBE           |              | 10.0    | 10.0  | 10.0  | 10.0    | 10.0  | 10.0   | 10.0  | 10.0  |
| Olfine STG       |              | 0.8     | 0.8   | 0.8   | 0.8     | 0.8   | 0.8    | 0.8   | 0.8   |
| Olfine E1010     |              | 10.0    | 10.0  | 10.0  | 10.0    | 10.0  | 10.0   | 10.0  | 10.0  |
| グリセリン            |              | 10.0    | 10.0  | 10.0  | 10.0    | 10.0  | 10.0   | 10.0  | 10.0  |
| 2-ヒドリドン          |              | 8.0     | 8.0   | 8.0   | 8.0     | 8.0   | 8.0    | 8.0   | 8.0   |
| DEG              |              | 0.9     | 0.9   | 0.9   | 0.9     | 0.9   | 0.9    | 0.9   | 0.9   |
| TEA              |              | 0.3     | 0.3   | 0.3   | 0.3     | 0.3   | 0.3    | 0.3   | 0.3   |
| Urea             |              | 残量      | 残量    | 残量    | 残量      | 残量    | 残量     | 残量    | 残量    |
| Proxel XL-2      |              |         |       |       |         |       |        |       |       |
| H <sub>2</sub> O |              |         |       |       |         |       |        |       |       |

[0028] Furthermore, 6 sets was prepared as 16 sets and an example of comparison by making combination of black ink and color ink into an example from each above-mentioned ink.

[0029] In evaluation, using the on-demand type ink-jet recording device of 360dpi and 48 nozzles which is the experimental model of our company, one line was first smeared away in color ink to a PPC form (Xerox Corp. registered trademark PPC form), recycled paper (the Honshu Paper registered trademark and \*\*\*\*\*), bond paper (Mead registered trademark Gilbert bond 25% cotton rag paper), and paper of fine quality (Oji Paper registered trademark O.K. paper of fine quality L), and, subsequently to a it top, the alpha character etc. was printed in black ink to them. Moreover, test patterns, such as an alpha character, were printed, respectively, using color ink and black ink independently. Evaluation of the following tests 1 and a test 2 was performed using the printing sample obtained by the above-mentioned method.

[0030] (Test 1) The bleeding prevention effect printing sample was observed by viewing, quality, such as existence of the bleeding between black colors, was evaluated, and the result was classified as follows.

O : bleeding is not accepted at all.

O : bleeding is hardly conspicuous.

x: Bleeding is conspicuous.

[0031] (Test 2) The bleeding prevention effect printing sample was observed by viewing, existence, such as black in a monochrome printing area, bleeding of each color, and a mustache, was evaluated, and the result was classified as follows.

O : it bleeds and a mustache is hardly accepted.

O : it bleeds and a mustache is accepted a little.

x: Bleed and a mustache is conspicuous.

[0032] An evaluation result is shown in Table 3.

[0033]

[Table 3]

|        | インクの組み合わせ |        | プリード防止効果判定 |     |      |     | にじみ防止効果判定 |     |
|--------|-----------|--------|------------|-----|------|-----|-----------|-----|
|        | ブラックインク   | カラーインク | PPC用紙      | 再生紙 | ボンド紙 | 上質紙 | ブラック      | カラー |
| 実施例 1  | B 1       | Y 2    | ○          | ○   | ○    | ○   | ◎         | ○   |
| 実施例 2  | B 1       | M 2    | ○          | ○   | ○    | ○   | ◎         | ○   |
| 実施例 3  | B 1       | C 3    | ○          | ○   | ○    | ○   | ◎         | ○   |
| 実施例 4  | B 2       | Y 1    | ○          | ○   | ○    | ○   | ○         | ◎   |
| 実施例 5  | B 2       | Y 3    | ○          | ○   | ○    | ○   | ○         | ◎   |
| 実施例 6  | B 2       | M 1    | ○          | ○   | ○    | ○   | ○         | ◎   |
| 実施例 7  | B 2       | C 1    | ○          | ○   | ○    | ○   | ○         | ◎   |
| 実施例 8  | B 2       | C 2    | ○          | ○   | ○    | ○   | ○         | ◎   |
| 実施例 9  | B 3       | Y 1    | ◎          | ◎   | ◎    | ◎   | ○         | ◎   |
| 実施例 10 | B 3       | M 1    | ◎          | ◎   | ◎    | ◎   | ○         | ◎   |
| 実施例 11 | B 3       | C 1    | ◎          | ◎   | ◎    | ◎   | ○         | ◎   |
| 実施例 12 | B 3       | C 2    | ◎          | ◎   | ◎    | ◎   | ○         | ◎   |
| 実施例 13 | B 4       | Y 1    | ◎          | ◎   | ◎    | ◎   | ◎         | ◎   |
| 実施例 14 | B 4       | M 1    | ◎          | ◎   | ◎    | ◎   | ◎         | ◎   |
| 実施例 15 | B 4       | C 1    | ◎          | ◎   | ◎    | ◎   | ◎         | ◎   |
| 実施例 16 | B 4       | C 2    | ◎          | ◎   | ◎    | ◎   | ◎         | ◎   |
| 比較例 1  | B 2       | Y 2    | ×          | ×   | ×    | ×   | ○         | ×   |
| 比較例 2  | B 2       | M 2    | ×          | ×   | ×    | ×   | ○         | ○   |
| 比較例 3  | B 2       | C 3    | ×          | ×   | ×    | ×   | ○         | ○   |
| 比較例 4  | B 3       | Y 2    | ×          | ×   | ×    | ×   | ×         | ○   |
| 比較例 5  | B 3       | M 2    | ×          | ×   | ×    | ×   | ×         | ○   |
| 比較例 6  | B 3       | C 3    | ×          | ×   | ×    | ×   | ×         | ○   |

[0034] The color ink-jet record method which is the color ink-jet record method of this invention, i.e., the color ink-jet record method using the ink of two or more colors which become including water, a color, a hydrophilic quantity boiling point low volatile solvent, polyhydric-alcohol low-grade alkyl ether, and the acetylene glycol expressed with the above-mentioned general formula, at least, and is characterized by black ink and/or color ink containing an auriferous color as a coloring agent is used so that clearly from Table 3. It is not based on the kind of recorded agent (regular paper), but the high-definition picture which does not have bleeding at the time of black color color mixture record is acquired. Moreover, when black ink or color ink contains an auriferous color as mentioned above, bleeding, a mustache, etc. at the time of monochrome printing are suppressed, and a high definition picture is acquired.

[0035]

[Effect of the Invention] By using the ink set for ink-jet record of this invention, the quality picture by which it is not based on the kind of recorded agent (regular paper), there is no bleeding between black ink color ink, and bleeding, a mustache, etc. at the time of monochrome printing were suppressed can be acquired.

[0036] For this reason, in order that it is not necessary to choose the kind of recorded agent (regular paper) and there may not be expensive special paper and the need of using a form chiefly, it also has the effect that a low running cost is realizable.

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**TECHNICAL FIELD**

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[The technical field to which invention belongs] this invention relates to the formation method of a color picture, and the color ink-jet record method of having used two or more primary color record liquid in more detail.

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PRIOR ART

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[Description of the Prior Art] As a result of in the color ink-jet record which generally piles up and prints each color of yellow, a Magenta, and cyanogen the ink which are liquids carrying out color mixture mutually or flowing out, bleeding, a mustache, etc. occur and the big technical problem that a quality of printed character deteriorates exists.

[0003] Then, in order to solve the above-mentioned technical problem conventionally, the surface tension of the record liquid of each color which forms a color picture should set at 20 degrees C like JP,60-197778,A. It is within the limits of 30 – 60 dyn/cm, and the fixing business time of the record liquid of each color to a recorded material and a bleeding degree are made equal by using that to which the surface tension of the record liquid of each color was equal, and the method of suppressing degradation of a color picture is proposed. However, by the method using the aforementioned record ink, the degree of bleeding of a record object does not decrease and cannot become a means to improve picture degradation. Moreover, in color printing containing especially the color mixture section, the bleeding of the ink between black colors occurs and the yet sufficiently high definition color ink-jet record method cannot be realized.

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**EFFECT OF THE INVENTION**

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[Effect of the Invention] By using the ink set for ink-jet record of this invention, the quality picture by which it is not based on the kind of recorded agent (regular paper), there is no bleeding between black ink color ink, and bleeding, a mustache, etc. at the time of monochrome printing were suppressed can be acquired.

[0036] For this reason, in order that it is not necessary to choose the kind of recorded agent (regular paper) and there may not be expensive special paper and the need of using a form chiefly, it also has the effect that a low running cost is realizable.

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**TECHNICAL PROBLEM**

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[Problem(s) to be Solved by the Invention] Then, especially the place made into the purpose of this invention is to offer the color ink-jet record method that the bleeding at the time of color printing is prevented, and a sharp and clear picture can be offered. Furthermore, it is not based on the kind of regular paper, but bleeds also at the time of color record and monochrome record of only black, and is in performing beardless high definition printing.

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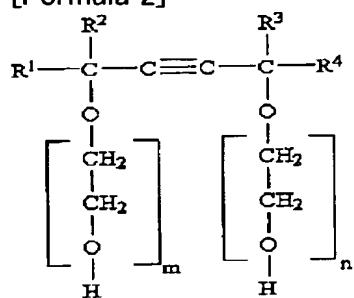
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## MEANS

[Means for Solving the Problem] In order that this invention persons may solve the above-mentioned technical problem, as a result of repeating examination wholeheartedly, at least Water, In the color ink-jet record method using the ink of two or more colors which come to contain a color, a hydrophilic quantity boiling point low volatile solvent, polyhydric-alcohol low-grade alkyl ether, and the acetylene glycol expressed with the following general formula When black ink and/or color ink contained an auriferous color as a coloring agent, the bleeding between black ink color ink was suppressed, and it found out that a sharp and clear picture was acquired.

[0006]

[Formula 2]



[0007] (Here, R1, R2, R3, and R4 express independently the alkyl group of carbon numbers 1-6, respectively, and n+m expresses 0-30)

When the coloring agent of black ink contains  $-COO-$  as a functional group in the further above-mentioned case, the bleeding between black ink color ink is prevented more effectively.

[0008] Moreover, when black ink contains a pigment in the state of distribution, the higher bleeding prevention effect is realized.

[0009] Furthermore, bleeding, a mustache, etc. at the time of monochrome printing were suppressed, and this invention persons found out that a high definition picture was acquired, when black ink or color ink contained an auriferous color as mentioned above.

[0010]

[Embodiments of the Invention] this invention is explained in detail. The auriferous color which the color ink used by the color ink-jet record method of this invention contains at least water, a color, a hydrophilic quantity boiling point low volatile solvent, polyhydric-alcohol low-grade alkyl ether, and the acetylene glycol expressed with the above-mentioned general formula, and has a transition-metals atom in a molecule as a color is used. In this case, although the above-mentioned bleeding prevention effect is realized even if it uses an auriferous color independently as a coloring agent, the same effect is acquired, when two or more auriferous colors are included in ink or an auriferous color and a non-auriferous color are mixed and included.

[0011] this invention person etc. reasons as follows the reason for having the effect that an auriferous color suppresses color bleeding as mentioned above. That is, although an auriferous color is divided roughly into what has transition metals at the center of a molecule like a phthalocyanine, and the thing which the metal has configurated for example, in azo combination

etc., in any case, generally the metal atom circumference has a high hydrophobic property, and since it is a water soluble dye, a hydrophilic radical exists in addition to the metal atom circumference. Therefore, generally compared with a non-auriferous color, it is considered by a hydrophilic target and the canal-interaction for an auriferous color to have the strong cohesive force between molecules. When ink is printed on a recorded material, the auriferous color with the strong interaction between molecules succeeds in condensation structure, and in order to prevent other colors etc. invading, the high bleeding prevention effect is demonstrated.

Moreover, since the cohesive force between molecules is strong, it is thought that it is hard to produce bleeding, a mustache, etc. also at the time of monochrome printing.

[0012] As an auriferous \*\*\*\*\* non-auriferous coloring agent used in the color ink-jet record method of this invention, pigments (graft carbon etc.) which processed the pigment front face by the resin etc. further, such as direct dye, acid dye, the food color, basic dye, a disperse dye, a vat dye, a solubilized vat dye, a reaction disperse dye, fat dye and an inorganic pigment (carbon black), and an organic pigment (insoluble azo pigment, soluble azo pigment, a phthalocyanine system pigment, an isoindolinone system pigment, a Quinacridone system pigment, \*\* RINON, perylene system pigment), can be used In this, especially a water soluble dye is desirable on the performance of ink. Specifically C. — I. direct red 2, 4, 9, 16, 23, 26, 31, 39, 62, 63, 72, 75, 76, 79, 80, 81, 83, 84, 89, 92, 95, 111, 173, 184, 207, 211, 212, 214, 218, 221, 223, 224, 225, 226, 227, 232, 233, 240, 241, 242, 243, 247, C.I. direct violet 7, 9, 47, 48, 51, 66, 90, 93, 94, 95, 98, 100, 101, C.I. direct yellow 8, 9, 11, 12, 27, 28, 29, 33, 35, 39, 41, 44, 50, 53, 58, 59, 68, 86, 87, 93, 95, 96, 98, 100, 106, 108, 109, 110, 130, 132, 142, 144, 161, 163, C.I. direct blue 1, 10, 15, 22, 25, 55, 67, 68, 71, 76, 77, 78, 80, 84, 86, 87, 90, 98, 106, 108, 109, 120, 151, 156, 158, 159, 160, 168, 189, 192, 193, 194, 199, 200, 201, 202, 203, 207, 211, 213, 214, 218, 225, 229, 236, 237, 244, 248, 249, 251, 252, 264, 270, 280, 288, 289, 291, C.I. direct black 9, 17, 19, 22, 32, 51, 56, 62, 69, 77, 80, 91, 94, 97, 108, 112, 113, 114, 117, 118, 121, 122, 125, 132, 146, 154, 166, 168, 173, 199, C.I. acid red 35, 42, 52, 57, 62, 80, 82, 111, 114, 118, 119, 127, 128, 131, 143, 151, 154, 158, 184249, 254, 257, 261, 263, 266, 289, 299, 301, 305, 336, 337, 361, 396, 397, and C.I. acid violet 5, 34, 43, 47, 48, 90, 103, 126, C.I. acid yellow 17, 19, 23, 25, 40, 42, 44, 49, 50, 61, 64, 76, 79, 105, 110, 127, 135, 143, 151, 159, 169, 174, 190, 195, 196, 197, 199, 218, 219, 222, 227, and C.I. acid blue 9, 25, 40, 41, 62, 72, 76, 78, 80, 82, 92, 106, 112, 113, 120, 127:1, 129, 138, 143, 175, 181, 205, 207, 220, 221, 230, 232, 247, 258, 260, 264, 271, 277, 278, 279, 280, 288, 290, 326, C.I. acid black 7, 24, 29, 43, 48, 52:1, 172, C.I. reactive red 3, 13, 17, 19, 21, 22, 23, 24, 29, 35, 37, 40, 41, 43, 45, 49, 55, and C.I. reactive violet 1, 3, 4, 5, 6, 7, 8, 9, 16, 17, 22, 23, 24, 26, 27, 33, 34, C.I. reactive yellow 2, 3, 13, 14, 15, 17, 18, 23, 24, 25, 26, 27, 29, 35, 37, 41, 42, C. — I. reactive blue 2, 3, 5, 8, 10, 13, 14, 15, 17, 18, 19, 21, 25, 26, 27, 28, 29, 38, and C.I. reactive black 4, 5, 8, 14, 21, 23, 26, 31, 32, 34, and C.I. basic red 12, 13, 14, 15, 18, 22, 23, 24, 25, 27, 29, 35, 36, 38, 39, 45, 46, C.I. basic violet 1, 2, 3, 7, 10, 15, 16, 20, 21, 25, 27, 28, 35, 37, 39, 40, 48, C. — I. basic yellow 1, 2, 4, 11, 13, 14, 15, 19, 21, 23, 24, 25, 28, 29, 32, 36, 39, 40, C.I. basic blue 1, 3, 5, 7, 9, 22, 26, 41, 45, 46, 47, 54, 57, 60, 62, 65, 66, 69, 71, C. I. basic black 8 etc. is mentioned.

[0013] As a content of the auriferous \*\*\*\*\* auriferous coloring agent in an ink composition part, in consideration of the printing concentration of a record object, clogging, a regurgitation property, etc., it is the range of 0.2 – 15wt% in a solid content as the sum total of all the coloring agents in ink, and is the range of 0.5 – 10wt% preferably.

[0014] As a hydrophilic quantity boiling point low volatile solvent used for this invention A glycerol, ethylene glucohol, a diethylene glycol, a triethylene glycol, A propylene glycol, a dipropylene glycol, a hexylene glycol, The polyhydric alcohol of high boiling point low volatility, such as a polyethylene glycol and a polypropylene glycol, is used. In addition, an N methyl 2-pyrrolidone, 1, 3-dimethyl imidazolidinone, Monoethanolamine, N, and N-dimethylethanolamine, N, and N-diethyl ethanolamine, Water-soluble organic solvents, such as nitrogen-containing organic solvents, such as an N-n-butyl diethanolamine, tri-isopropanolamine, and a triethanolamine, can be added in the range which bleeding of printing does not produce. A diethylene glycol, a glycerol, etc. are especially desirable. although it is common knowledge that these hydrophilic quantity boiling point low volatile solvents are added as a moisturizer for clogging prevention etc. — the greatest effect as an indispensable component of this invention — a member — it is in relief of

pervasion nature the case where volatile components, such as water, evaporate on the inside of a head, an ink supply way, etc. by unusual situation generating especially according to failure of a printer etc. — the member of polyhydric-alcohol low-grade alkyl ether — pervasion nature is eased

[0015] moreover — as the desirable example of the polyhydric-alcohol low-grade alkyl ether used for this invention — monochrome, JI, and a triethylene glycol C — one to 6 alkyl ether, the triethylene-glycol monobutyl ether, the diethylene-glycol monobutyl ether, a diethylene glycol monoethyl ether, the diethylene-glycol monomethyl ether, the propylene-glycol monobutyl ether, etc. are mentioned more preferably, and it is the triethylene-glycol monobutyl ether most preferably This addition is 7 – 10wt% preferably [ that it is 7 – 12wt% ] and more preferably.

[0016] Moreover, the acetylene glycol expressed with the above-mentioned general formula must be contained in the ink used by this invention. If the desirable example of an acetylene glycol is given, it will be as in Table 1.

[0017]

[Table 1]

|       | R <sup>1</sup> | R <sup>2</sup> | R <sup>3</sup> | R <sup>4</sup> | n+m |
|-------|----------------|----------------|----------------|----------------|-----|
| No. 1 | iso-ブチル        | メチル            | メチル            | iso-ブチル        | 1.0 |
| No. 2 | iso-ブチル        | メチル            | メチル            | iso-ブチル        | 3.5 |
| No. 3 | エチル            | メチル            | メチル            | エチル            | 1.0 |
| No. 4 | メチル            | メチル            | メチル            | メチル            | 0   |
| No. 5 | エチル            | メチル            | メチル            | エチル            | 0   |
| No. 6 | iso-ブチル        | メチル            | メチル            | iso-ブチル        | 0   |

[0018] The acetylene glycol of No.1 in Table 1 is the most desirable.

[0019] These acetylene glycols can use what is marketed, for example, can use ORUFIN E1004, E1010, and STG, SAFI Norian 82 (manufacturer : Air Product and Chemicals, Inc., a selling agency : Shin-Etsu Chemical Co., Ltd.), etc.

[0020] The addition of an acetylene glycol is 0.5 – 1wt% preferably [ that it is 0.5 – 1.2wt% ] and more preferably.

[0021] By using combining polyhydric-alcohol low-grade alkyl ether and an acetylene glycol with the above-mentioned addition, quick-drying [ of an ink constituent ] is improved and degradation of the quality of printed character by bleeding, color mixture, etc. can be prevented.

Furthermore, although the phenomenon which erodes the resin which constitutes a recording head and ink passage will often be observed if polyhydric-alcohol low-grade alkyl ether is used by independent [ it ], it is combining with an acetylene glycol and such an erosion phenomenon can also be prevented. furthermore, the above-mentioned hydrophilic quantity boiling point low volatile solvent — polyhydric-alcohol low-grade alkyl ether — receiving — more than the 50wt% — the effect is more improvable by adding

[0022] In addition, in the record ink used for the ink set for color ink-jet record of this invention, a well-known dispersant, a surfactant, a viscosity modifier, a surface tension modifier, a specific resistance modifier, pH modifier, an antioxidant, an antifungal agent, a chelating agent, etc. can be added if needed conventionally.

[0023] Although the contents in the ink composition part of these various additives differ according to the purpose, as for an excessive amount, it is desirable to foam and to use it in 0.001 – 5wt% from causes, such as a deposit and shelf-life degradation, and a bird clapper.

[0024] Although the content of the water used by this invention is determined in the latus range depending on the kind of the above-mentioned solvent component, additive, etc., a content, and the property of ink for which it asks, in the record liquid whole quantity, generally it is 40 – 95wt%, and the range of it is 65 – 95wt% more preferably.

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EXAMPLE

[Example] An example and the example of comparison are used for below, and the color ink-jet record method of this invention is further explained to it.

[0026] Composition of the ink used for the evaluation mentioned later first is summarized in Table 2. the number in Table 2 -- all -- a weight criteria % display -- it is -- a residue -- the whole -- 100% -- \*\* -- it means adding pure water so that it may become After mixing each component of Table 2 and agitating and dissolving at 25 degrees C for 2 hours, using the membrane filter (Advantech registered trademark) of the diameter of 0.8 micrometer, the pressure filtration of kg [ 2 / ] was carried out by the pressure of 2 cm, and each ink was obtained. In addition, although both the direct blacks 154 and direct blacks 90 of front Naka are non-auriferous colors, the former has -COO- as a functional group and the latter does not have them. Moreover, since carbon black has mainly embellished the front face with -COO-, it is making the stable distributed state in ink, without otherwise adding a dispersant etc.

[0027]

[Table 2]

|                  |              | ブラック インク |       |       |       |
|------------------|--------------|----------|-------|-------|-------|
|                  |              | インクB1    | インクB2 | インクB3 | インクB4 |
| 含金染料             | アシッドブラック43   | 2.0      |       |       |       |
| 非含金染料            | ダイレクトブラック90  |          | 2.0   |       |       |
|                  | ダイレクトブラック154 |          |       | 2.0   |       |
| 表面処理顔料           | カーボンブラック     |          |       |       | 2.0   |
| TEGmBE           |              | 10.0     | 10.0  | 10.0  | 10.0  |
| Ol fine STG      |              | 0.8      | 0.8   | 0.8   | 0.8   |
| グリセリン            |              | 9.0      | 9.0   | 9.0   | 9.0   |
| 2-ヒドロイソブチル       |              | 4.0      | 4.0   | 4.0   | 4.0   |
| TEA              |              | 0.9      | 0.9   | 0.9   | 0.9   |
| Proxel XL-2      |              | 0.3      | 0.3   | 0.3   | 0.3   |
| H <sub>2</sub> O |              | 残量       | 残量    | 残量    | 残量    |

|                  |             | イエローアイント |       | マゼンタ インク |       | シアン インク |       |       |       |
|------------------|-------------|----------|-------|----------|-------|---------|-------|-------|-------|
|                  |             | インクY1    | インクY2 | インクY3    | インクM1 | インクM2   | インクC1 | インクC2 | インクC3 |
| 含金染料             | ダイレクトイエロー39 | 3.0      |       | 2.0      |       |         |       |       |       |
|                  | アシッドレッド184  |          |       |          |       | 3.0     |       |       |       |
|                  | ダイレクトブルー199 |          |       |          |       |         | 3.0   |       |       |
|                  | ダイレクトブルー202 |          |       |          |       |         |       | 3.0   |       |
| 非含金染料            | アシッドイエロー105 |          | 3.0   | 1.0      |       | 3.0     |       |       |       |
|                  | ダイレクトレッド16  |          |       |          |       | 3.0     |       |       |       |
|                  | ダイレクトブルー120 |          |       |          |       |         |       | 3.0   |       |
| TEGmBE           |             | 10.0     | 10.0  | 10.0     | 10.0  | 10.0    | 10.0  | 10.0  | 10.0  |
| Ol fine STG      |             | 0.8      | 0.8   | 0.8      | 0.8   | 0.8     | 0.8   | 0.8   | 0.8   |
| Ol fine E1010    |             | 10.0     | 10.0  | 10.0     | 10.0  | 10.0    | 10.0  | 10.0  | 10.0  |
| グリセリン            |             | 10.0     | 10.0  | 10.0     | 10.0  | 10.0    | 10.0  | 10.0  | 10.0  |
| 2-ヒドロイソブチル       |             | 8.0      | 8.0   | 8.0      | 8.0   | 8.0     | 8.0   | 8.0   | 8.0   |
| DEG              |             | 0.9      | 0.9   | 0.9      | 0.9   | 0.9     | 0.9   | 0.9   | 0.9   |
| TEA              |             |          |       |          | 3.5   | 3.5     |       |       |       |
| Urea             |             |          |       |          |       | 3.5     |       |       |       |
| Proxel XL-2      |             | 0.3      | 0.3   | 0.3      | 0.3   | 0.3     | 0.3   | 0.3   | 0.3   |
| H <sub>2</sub> O |             | 残量       | 残量    | 残量       | 残量    | 残量      | 残量    | 残量    | 残量    |

[0028] Furthermore, 6 sets was prepared as 16 sets and an example of comparison by making combination of black ink and color ink into an example from each above-mentioned ink.

[0029] In evaluation, using the on-demand type ink-jet recording device of 360dpi and 48 nozzles which is the experimental model of our company, one line was first smeared away in color ink to a PPC form (Xerox Corp. registered trademark PPC form), recycled paper (the Honshu Paper registered trademark and \*\*\*\*\*), bond paper (Mead registered trademark Gilbert bond 25%

cotton rag paper), and paper of fine quality (Oji Paper registered trademark O.K. paper of fine quality L), and, subsequently to a fit top, the alpha character etc. was printed in black ink to them. Moreover, test patterns, such as an alpha character, were printed, respectively, using color ink and black ink independently. Evaluation of the following tests 1 and a test 2 was performed using the printing sample obtained by the above-mentioned method.

[0030] (Test 1) The bleeding prevention effect printing sample was observed by viewing, quality, such as existence of the bleeding between black colors, was evaluated, and the result was classified as follows.

O : bleeding is not accepted at all.

O : bleeding is hardly conspicuous.

x: Bleeding is conspicuous.

[0031] (Test 2) The bleeding prevention effect printing sample was observed by viewing, existence, such as black in a monochrome printing area, bleeding of each color, and a mustache, was evaluated, and the result was classified as follows.

O : it bleeds and a mustache is hardly accepted.

O : it bleeds and a mustache is accepted a little.

x: Bleed and a mustache is conspicuous.

[0032] An evaluation result is shown in Table 3.

[0033]

[Table 3]

|       | インクの組み合わせ |        | プリート防止効果判定 |     |      |     | にじみ防止効果判定 |     |
|-------|-----------|--------|------------|-----|------|-----|-----------|-----|
|       | ブラックインク   | カラーインク | PPC用紙      | 再生紙 | ボンド紙 | 上質紙 | ブラック      | カラー |
| 実施例1  | B1        | Y2     | ○          | ○   | ○    | ○   | ◎         | ○   |
| 実施例2  | B1        | M2     | ○          | ○   | ○    | ○   | ◎         | ○   |
| 実施例3  | B1        | C3     | ○          | ○   | ○    | ○   | ◎         | ○   |
| 実施例4  | B2        | Y1     | ○          | ○   | ○    | ○   | ○         | ○   |
| 実施例5  | B2        | Y3     | ○          | ○   | ○    | ○   | ○         | ○   |
| 実施例6  | B2        | M1     | ○          | ○   | ○    | ○   | ○         | ○   |
| 実施例7  | B2        | C1     | ○          | ○   | ○    | ○   | ○         | ○   |
| 実施例8  | B2        | C2     | ○          | ○   | ○    | ○   | ○         | ○   |
| 実施例9  | B3        | Y1     | ◎          | ◎   | ◎    | ◎   | ○         | ○   |
| 実施例10 | B3        | M1     | ◎          | ◎   | ◎    | ◎   | ○         | ○   |
| 実施例11 | B3        | C1     | ◎          | ◎   | ◎    | ◎   | ○         | ○   |
| 実施例12 | B3        | C2     | ◎          | ◎   | ◎    | ◎   | ○         | ○   |
| 実施例13 | B4        | Y1     | ◎          | ◎   | ◎    | ◎   | ◎         | ◎   |
| 実施例14 | B4        | M1     | ◎          | ◎   | ◎    | ◎   | ◎         | ◎   |
| 実施例15 | B4        | C1     | ◎          | ◎   | ◎    | ◎   | ◎         | ◎   |
| 実施例16 | B4        | C2     | ◎          | ◎   | ◎    | ◎   | ◎         | ◎   |
| 比較例1  | B2        | Y2     | ×          | ×   | ×    | ×   | ○         | ×   |
| 比較例2  | B2        | M2     | ×          | ×   | ×    | ×   | ○         | ○   |
| 比較例3  | B2        | C3     | ×          | ×   | ×    | ×   | ○         | ○   |
| 比較例4  | B3        | Y2     | ×          | ×   | ×    | ×   | ×         | ○   |
| 比較例5  | B3        | M2     | ×          | ×   | ×    | ×   | ×         | ○   |
| 比較例6  | B3        | C3     | ×          | ×   | ×    | ×   | ×         | ○   |

[0034] The color ink-jet record method which is the color ink-jet record method of this invention, i.e., the color ink-jet record method using the ink of two or more colors which become including water, a color, a hydrophilic quantity boiling point low volatile solvent, polyhydric-alcohol low-grade alkyl ether, and the acetylene glycol expressed with the above-mentioned general formula, at least, and is characterized by black ink and/or color ink containing an auriferous color as a coloring agent is used so that clearly from Table 3. It is not based on the kind of recorded agent (regular paper), but the high-definition picture which does not have bleeding at the time of black color color mixture record is acquired. Moreover, when black ink or color ink contains an auriferous color as mentioned above, bleeding, a mustache, etc. at the time of monochrome printing are suppressed, and a high definition picture is acquired.

[Translation done.]